The phase space structure of supercooled liquids: Evidence of a dynamical critical temperature.

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(February 1, 2008)

We calculate local potential energy minima (inherent structures) for a simple model of orthoterphenyl (OTP), from computer simulations over a wide temperature range. We show that the results are very sensitive to the system size. We locate, from the temperature and size dependence of inherent structure energies, a well defined cross-over temperature that corresponds to the dynamical critical temperature predicted by mode coupling theory and in mean field spin glass models. Comparing the known phase space structure of mean field p-spin models and the present results for the OTP model, we find evidence supporting the proposed similarity between glass-forming liquids and a class of spin glass models.

PACS numbers:64.70.Pf,61.20.Gy, 61.20.Ja

The idea that essential features of glass formation from supercooled liquids [1,2] may be contained in the behavior of spin glass models has been actively pursued in recent years, with a focus on mean field p-spin models [3–7]. In particular, the dynamical ideal mode coupling theory (MCT) for supercooled liquids [8] and the disordered mean field p-spin models, with $p > 2$ display many common features observed in structural glasses. Both approaches predict, on cooling the system, the existence of a dynamical critical temperature (T_{MCT} in MCT language and T_D in p-spin language) at which, from a dynamical point of view, an ergodic to non-ergodic transition takes place. Below this temperature the system is dynamically frozen in a metastable state and confined in a finite region of phase space (basin, in the following). Relaxation to the true equilibrium state below this temperature takes place via activated processes, which are not taken into account dynamically in MCT and are absent in the mean field p-spin case, where all basins are separated by infinite barriers. Both theories make predictions for the time dependence of correlation functions (correlators). The evolution of correlation functions in the p-spin case coincides [4,6] with that obtained for the schematic MCT model [9]. In real structural glasses no sharp ergodic to non-ergodic transition is observed, due to the finite height of the barriers separating different basins, so that this dynamical critical temperature plays the role of crossover temperature between regions of different dynamical character. Specifically, it has been argued that below this crossover temperature, activated crossing of potential energy barriers, first suggested by Goldstein [10], becomes the dominant mechanism of diffusion [11]. MCT has been the subject of several tests above T_{MCT} and it has been shown to describe the space

and time dependence of correlators satisfactorily [12,13].

On the other hand, mean field p-spin models have the merit of offering a clear picture of the structure of phase space, in particular the aspects associated with the transition at T_D. The analytic solutions of the TAP equations [4,14] show that the region of phase space visited below T_D is composed by an exponentially large number of different basins, separated by infinitely high barriers. Different basins are unambiguously specified by the value of the energy at the minimum, E_{min}, which assume values only between a minimum value E_o and a maximum value E_{th}. Stationary solutions with E_{min} higher than E_{th} are unstable even at zero temperature. Below T_D, in thermodynamic equilibrium, basins with a well defined value of $E_{min}(T)$ are populated at each temperature.

The TAP solutions at $T = 0$ K coincide with the local phase space minima of the potential energy and are thus analog of the so-called inherent structures proposed by Stillinger [15] to describe the phase space structure of liquids. In Stillinger's approach, phase space is partitioned in basins such that steepest descent trajectories starting from any point in a basin converge to the same energy minimum, which defines the inherent structure configuration. Previous numerical studies of inherent structures in supercooled liquids have been confined to rather small system sizes and have rarely aimed at identifying the presence of an underlying dynamical critical temperature. A recent study of a Lennard-Jones binary mixture at constant density for a 256 atom sample [16] did not reveal any particular signature of the presence of a dynamical temperature in the T dependence of the inherent structure energies.

This Letter explores the possibility that the phase space structure of the liquid state is similar to that of p-

spin models. The work is based on a detailed study of the energy relaxation in phase space toward the minimum, starting from equilibrated independent configurations at a series of temperatures. The use of the conjugate gradient technique [17] guarantees an efficient monotonically decreasing path toward the minimum and of course the absence of basin change during minimization. The basic idea behind this work is that the equivalence between inherent structures of the liquid and TAP solutions facilitates the comparison of the phase space structure of structural glasses and of mean field p-spin models.

We perform a series of long molecular dynamics (MD) simulations for systems of different sizes ranging from 343 molecules (the smallest size compatible with the intermolecular potential range) up to 9261 molecules [18]. The selected intermolecular potential models the OTP molecule as a rigid structure composed of three sites. All site-site interactions are described by the same Lennard-Jones potential, whose parameters have been optimized to reproduce the properties of the liquid. For this potential $T_{MCT} = 280\,K$, a figure calculated from the T dependence of the non-ergodicity parameter [19]. Below T_{MCT}, the MD trajectories have been calculated for times up to 20 ns, to guarantee thermodynamic equilibrium and satisfactory sampling of phase space. Both static and dynamic quantities, evaluated along the MD trajectory, do not show any finite size effect. Several different equilibrium configurations, separated by more than the relaxation time have been used as starting points for the evaluation of the corresponding inherent structures by performing a standard conjugate gradient minimization. The energy minimization has been performed up to a relative precision of 10^{-12} to ensure a proper determination of the minimum.

Fig. 1 shows the potential energy during the minimization procedure at different temperatures. While for $T \leq 305\,K$ there is one single relaxation process to the minimum, with a characteristic "time" which has no system size dependence, at $T = 346\,K$ the relaxation to the minimum occurs in a two-step process. The first (size independent) relaxation process is followed by another slower relaxation which drives the system to a deeper and size dependent minimum. These data indicate that the system first relaxes quickly to a quasi-stable size independent point characterized by an energy $E_s(T)$ and then explores the possibility of finding a lower energy minimum configuration with value $E_{min}(T)$. Strikingly enough, the success of this search is strongly size dependent. Indeed, for the smallest system $E_s(T)$ coincides with $E_{min}(T)$. It is particularly important also to note that the change of behavior from size dependent to size independent relaxation to E_{min} occurs very close to the previously estimated T_{MCT}. In p-spin models, the energy E_{min} of the disordered solution (i.e. the stable solution for $T \geq T_D$) is equal to that of the first (highest) stable TAP solution. By extrapolating $E_{min}(T)$ vs $1/N$

for $1/N$ going to zero (see inset of Fig. 1 we find that $\lim_{N \to \infty} E_{min}(T = 346K)$ is close to $E_{min}(T = T_{MCT})$ which thus provides strong evidence for the identification of T_D with T_{MCT}.

In p-spin models, below T_D the energies of the relevant TAP minima lie below the threshold value E_{th}, and the curvature in phase space of these TAP solutions is positive in all directions. Stationary solutions with energies greater than E_{th} display unstable (or non-positive curvature) directions [20,7]. If this feature is preserved in the phase structure of supercooled liquids, one would predict that, in the thermodynamic limit, for $T > T_{MCT}$ there will be always a finite number of unstable directions for higher energy stationary points and during a local energy minimization, the system will always relax to E_{th}. But if the fraction of unstable directions f_u is sufficiently small, as it is close to T_{MCT}, in finite size systems there would be realizations of higher energy states which are stable. For finite size systems, only when $6Nf_u(T)$ is greater than one, i.e. only when statistically there will be at least one unstable solution, the system can abandon the saddle state and relax toward a lower energy minimum. To test the validity of this prediction, Fig. 2 shows the energy during the minimization procedure at a T close to T_{MCT} for all studied realizations of the large size system. For comparison, we show also the relaxation curves averaged over all realizations for the 343 molecules cases. Interestingly enough, a clear bimodal effect is observed. A fraction of the realizations relaxes to E_{min}, while the remaining fraction is trapped at the energy E_s. The smaller system on average relaxes to E_s. As suggested by Fig. 1, such system size dependence is seen only above the previously estimated T_{MCT} for this system. The size effects displayed in both figures, as well as the dichotomous behavior observed in Fig.2, suggests that T_{MCT} can be identified as the temperature at which the fraction of unstable directions in phase space $f_u(T = T_{MCT})$, evaluated at E_s, goes to zero from above. In Ref. [21], by analysing the instantaneous normal mode spectrum [22] in a deep supercooled liquid above T_{MCT}, it was shown that the fraction of truly unstable directions in phase space tends to vanish at T_{MCT}, strongly suggesting that the dynamics above and below T_{MCT} is dominated by different physical transport mechanisms: Above T_{MCT} the dynamics is controlled by the search of unstable directions while below it is controlled by activated processes. We believe that our present observations are relevant in establishing the nature of such a dynamical crossover.

Fig. 3 shows the temperature dependence of $E_s(T)$ and $E_{min}(T)$ for different system sizes. $E_s(T)$ does not show any significant dependence on the system size, suggesting that in searching for the minimum the system quickly finds a local phase space environment that does not depend on the system size. For T higher than a size dependent cross-over temperature, a secondary re-

laxation process appears – suggesting that statistically at least one direction in phase space at $E_s(T)$ is unstable, such that the system relaxes to the deeper energy minimum $E_{min}(T)$. The cross over temperature is size dependent and in the limit $1/N$ going to zero extrapolates to $T \sim 285K$ (see inset of Fig. 3), supporting the identification, in the thermodynamic limit, of this cross over temperature with T_{MCT}. Above the cross-over temperature there is a large T range where $E_{min}(T)$ is approximatively constant, suggesting that there is a well defined minimum characteristic energy of the liquid state above T_{MCT}. Below the crossover temperature the difference between $E_s(T)$ and $E_{min}(T)$ disappears. No finite size effects are present. The phase space visited in this T range is partitioned in many different basins. Interestingly enough, the variance in $E_{min}(T)$ is very small below the crossover temperature, supporting the view that in the thermodynamic limit, at each temperature, basins with a well defined value of $E_{min}(T)$ are populated. It is also worth noting that $E_s(T)$ is not only system size independent, but is an increasing function of T and coincides with E_{min} up to the crossover temperature for each system size. The size effects shown in Fig. 3 suggest the study of the phase space of the liquid not only in terms of minima, but also in terms of stationary points of higher order, as phase space features relevant to the system's dynamics. Finite dimensional cuts of the thermodynamic phase space (finite N) transform saddle points into local minima, altering the description of phase space as a more numerous collection of different basins. In the thermodynamic limit, only the region of phase space visited for $T < T_{MCT}$ can be described as a collection of different basins, in agreement with the description of the free energy of supercooled liquids proposed by Stillinger [15] and observed in the TAP solution of the p-spin models. Following the analogy with disordered p-spin models, we note that $E_{min}(T)$ correspond to the equilibrium TAP solutions. Interestingly, the finite size effect effects we report allow visualization of the equivalent of the TAP solutions for $E > E_{th}$, which have been shown to be unstable stationary states [20].

In summary, in this Letter we have presented results on the phase space structure of supercooled liquids (structural glasses) and discussed the analogies with disordered spin glasses. In particular (i) we have identified T_{MCT} in terms of a static property of the system, showing that in the thermodynamic limit, T_{MCT} corresponds to the temperature at which the T dependence of the inherent structure energy has a clear break. This suggests a possible experiment based on ultrafast quenches to determine the T_{MCT} for a liquid. (ii) we have shown evidence that above T_{MCT} the inherent structure energy is T-independent [23], suggesting the possibility of a unique basin characterizing the liquid. (iii) Above T_{MCT}, size effects become important due to the transformation of low dimensional saddle points to minima in finite systems.

The different structure of the phase space visited above and below T_{MCT} demonstrated by the present work offers precise hints about the difference of dynamical behavior above and below T_{MCT}. While below T_{MCT} the slowing down of dynamics on cooling can be connected to the time required to hop across energy barriers between basins, above T_{MCT} exploration of phase space can take place *via* unstable directions connecting different quasistable environments (defined by their value $E_S(T)$). This suggests further investigation of such quasi-stable solutions for their relevance to the dynamics above T_{MCT} [24].(iv) Finally, based on the formal equivalence between TAP solutions at $T = 0K$ and inherent structures, we have shown that the phase space structure of the present model liquid is consistent with the phase structure of the mean field p-spin models and have identified T_{MCT} with T_D.

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[23] We plan to study in the near future the T dependence of the inherent structures for T higher than the ones studied in this Letter. This requires a careful study due to the vicinity of the gas-liquid instability. We plan also to study a constant density path in the phase diagram.

[24] Indeed, it appears plausible that the onset of stretched exponential and non-Arrhenius behavior above T_{MCT} studied in [16] is related to $E_s(T)$, which is under current investigation.

FIG. 1. Relaxation of the potential energy per molecule during the minimization procedure for three different system sizes, starting from equilibrated configurations at three different temperatures $T = 266$, $T = 305$ and $T = 346$ K. Each curve is the average over several independent minimizations. Dotted line, $N = 343$; Full line $N = 1000$; Long Dashed $N = 9261$. The inset shows the inherent structure energy as a function of the inverse of the number of molecules N for $T = 305K$ (dashed line) and for $T = 346K$ (full line).

FIG. 2. Potential energy per molecule as a function of the number of steps in the conjgate gradient procedure when $N = 9261$. Different curves refer to different equilibrium configurations at $T = 318K$. The inset shows an enlarged view in the energy region around E_s (full lines) together with the averaged relaxation for $N = 343$ (long dashed).

FIG. 3. Temperature dependence of E_s (empty symbols) and E_{min} (filled symbols) as a function of temperature for three different system sizes. Square $N = 9261$; Circle $N = 1000$, Triangle $N = 343$. Lines ar drawn to guide the eye. It is important to note that (i) below 300 K, E_s coincides with E_{min}; (ii) at $T = 305K$ finite size effects hinder the second relaxation process also when $N = 9261$.
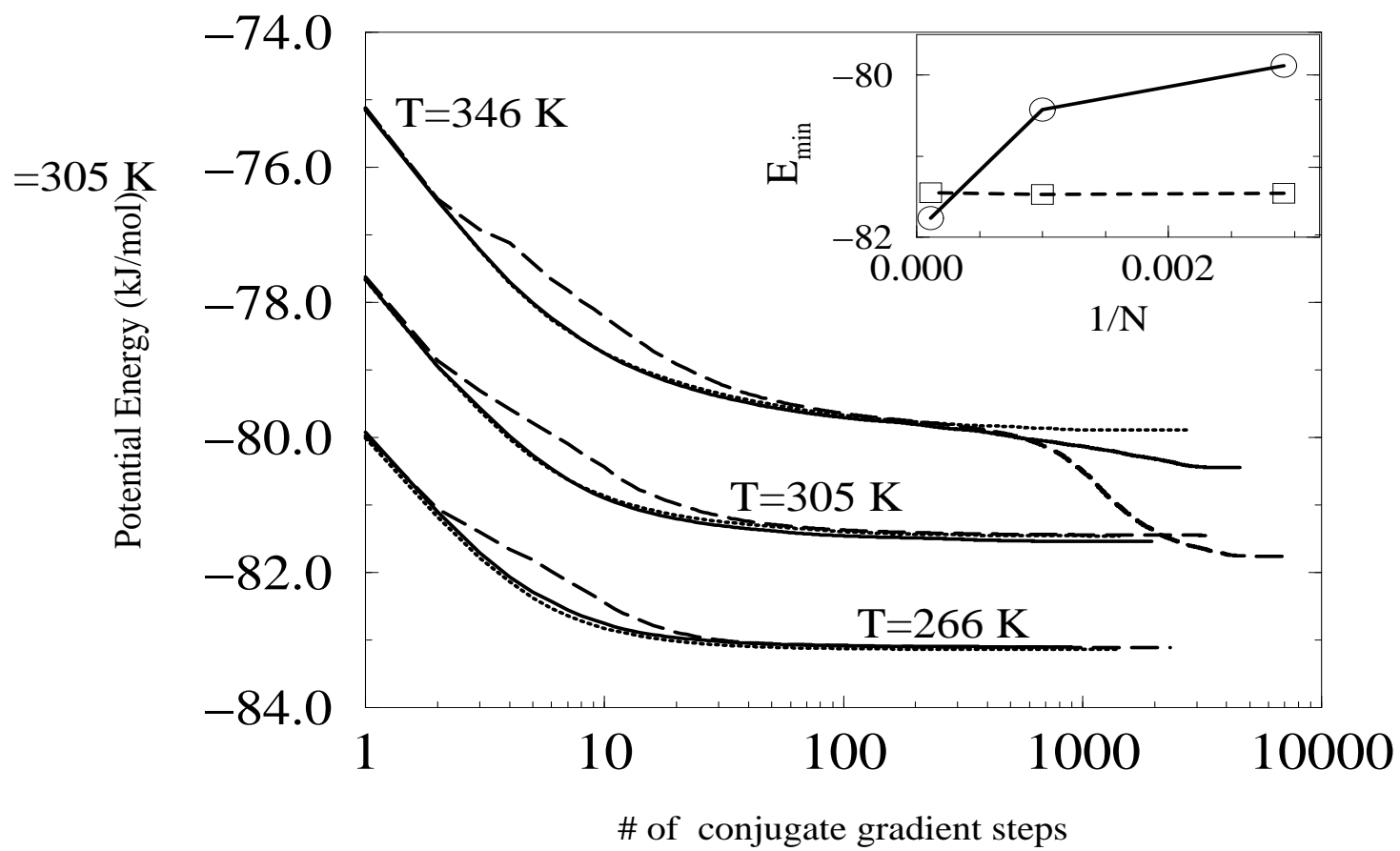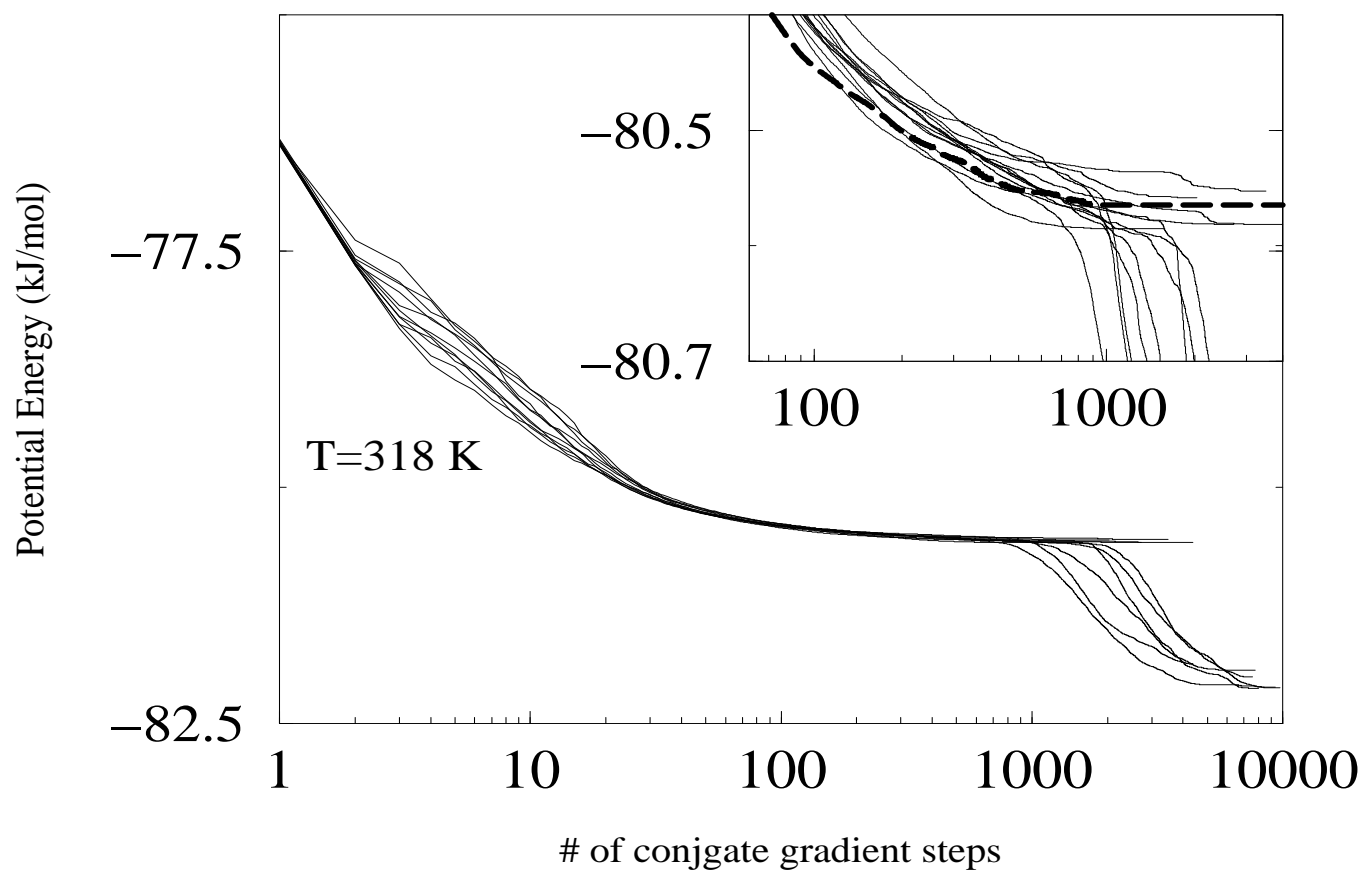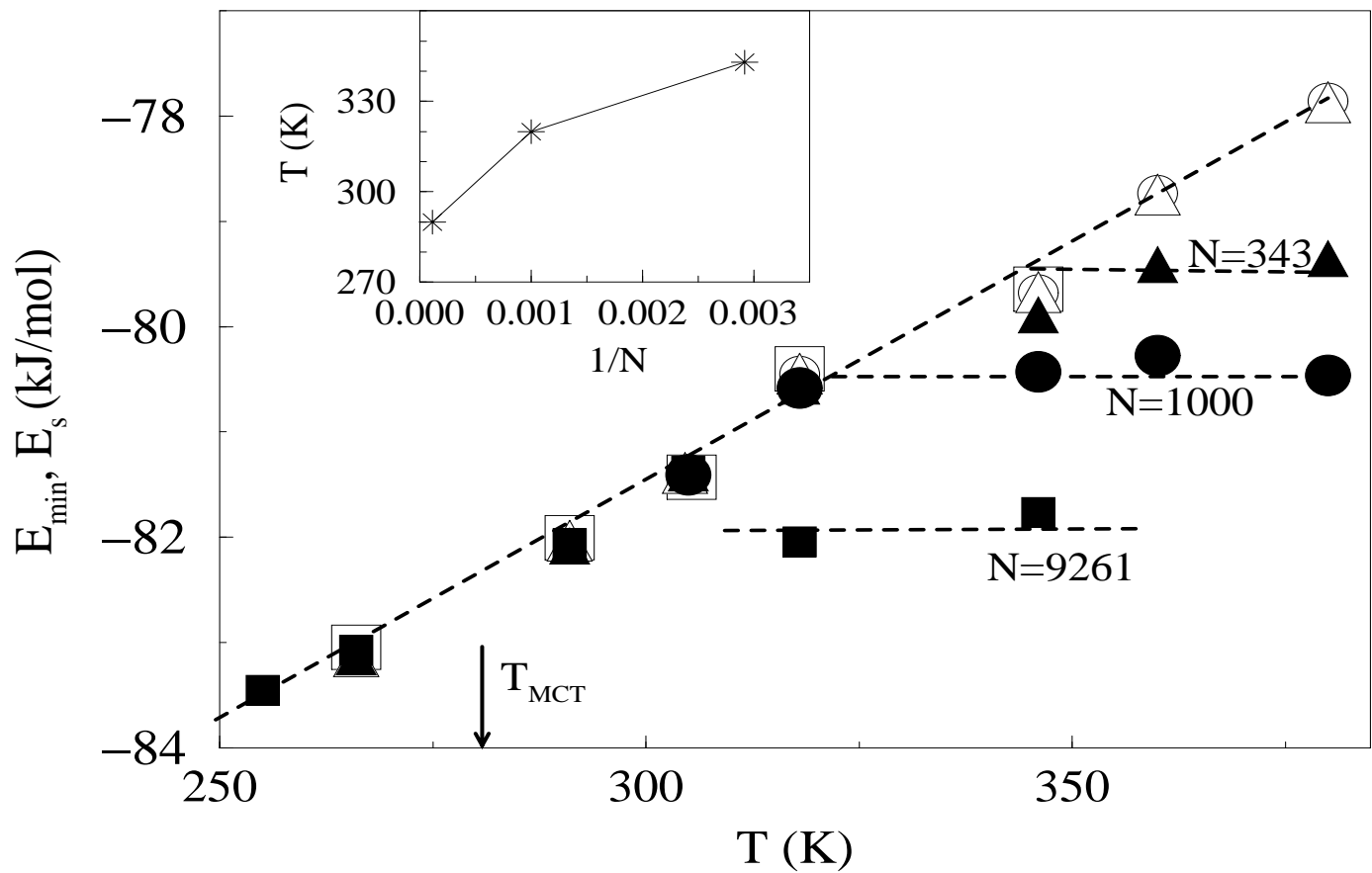
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